

# Non-equilibrium gelation transition in a kinetic lattice gas model

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**Abstract.** – We consider a lattice gas model which in addition to the canonical nearest neighbor pair interatomic interaction accounts for a many-body interaction inside atomic trios. Interactions of this kind arise in the coherent strained epitaxy and were recently used by us to describe some surface phenomena. With the use of the Monte Carlo simulation we show that in two dimensions the model at low temperature exhibits glassy behaviour, in particular, undergoes a gelation transition. We argue that this model may belong to the universality class of non-equilibrium critical phenomena which may comprise also some off-lattice structural glass transitions, provided such a class exists.

It seems to be firmly established that the glass transition which has been the subject of extensive study in recent years (see review papers [1,2,3]) does not belong to the category of the familiar equilibrium phase transitions but is a purely kinetic phenomenon which occurs in some many-body far from equilibrium systems (FFES) [1]. Thus, our poor understanding of glassy phenomena [4,2] can be related to the poor development of the non-equilibrium statistical physics in comparison with its equilibrium counterpart.

Historically, investigation of the non-equilibrium kinetics went in parallel with the equilibrium studies <sup>(1)</sup> but only for systems in the vicinity of equilibrium a systematic approach based on the linear response theory has been developed [5] while in the far from equilibrium case any technique of comparable generality is absent.

A major difficulty in developing a unified description of the FFES is their much larger diversity in comparison with the near-equilibrium ones <sup>(2)</sup> and that some of them are very complex, biological systems being the standard example. So it seems unrealistic to expect that a microscopic approach similar to LRT can be built which would be equally applicable to all FFES. Therefore, alongside with microscopic theories of individual FFES, phenomenological

<sup>(1)</sup>The famous Boltzmann equation (1872) appeared practically simultaneously with the modern formulation of the laws of thermodynamics.

<sup>(2)</sup>While near equilibrium systems in statistical terms can be considered as linear perturbations in the vicinity of a canonical equilibrium ensemble, the FFES comprise all other statistical ensembles.

approaches are being developed [6,3] based on simple lattice models aiming at a qualitative description of typical non-equilibrium behaviours observed in physically different systems. It is hoped that the number of such models is small [6,3] which would provide us with an efficient classification of far from equilibrium phenomena similar to the classification of the equilibrium critical phenomena according to their universality classes [7].

This approach looks as a natural candidate to attack the problem of the glass transition. Indeed, this phenomenon occurs in such disparate systems as metal alloys, polymer melts, biopolymer [1], colloidal suspensions [8,9], etc., that their unified microscopic description looks hopeless. On the other hand, the physics of the glassy phenomena is considered to be basically the same in all substances and their theoretical interpretation is being usually sought in a unified framework [2].

Presumably with this aim a number of lattice models of glassy phenomena have been proposed [3]. The main deficiency of the majority of those models is, in our opinion, that their definitions are not quite physical. For example, the model of Kob and Andersen [10] is based on microscopic dynamics defined by a set of rules designed to imitate the glassy behaviour. But the physical origin of these rules is not clear, especially taking into account that the kinetics do not change the system's energy. The recently proposed class of lattice glass models [11] replaces the dynamic constraints of ref. [10] by similar constraints on the local atomic density. In both cases the proposed rules are motivated by quite plausible physical arguments. But recently it was shown [12,13] that contrary to what one might expect on the basis of experience gained in dealing with equilibrium critical phenomena, in the far from equilibrium case even a seemingly innocent and commonly accepted simplification of microscopic dynamic rules can change the universality class of the non-equilibrium critical behaviour.

The aim of the present letter is to propose a model which is capable of describing a glass transition and at the same time is physical in the same sense as the canonical lattice gas model (LGM) with nearest neighbor interatomic interactions. The latter is equivalent to the Ising model which up to date is the most widely used model of both equilibrium and non-equilibrium phenomena. In our opinion, the unique status of the LGM/Ising model in statistical physics is largely due to the fact that while being extremely simple and thus very convenient for theoretical study, the model at the same time is quite physical in the sense that from the point of view of statistical physics it might have described a real system. Similarly, the stochastic dynamics commonly used in numerical simulations of FFES were shown [14] to be formally fully consistent with the statistical laws, hence also physically acceptable.

The hamiltonian of the model we are going to consider reads

$$H = \sum_{\mathbf{i}, \gamma} (V n_{\mathbf{i}} n_{\mathbf{i}+\gamma} + W n_{\mathbf{i}-\gamma} n_{\mathbf{i}+\gamma}), \quad (1)$$

where  $\gamma = \{\hat{e}_x, \hat{e}_y\}$  are the unit vectors of a square lattice. The parameters  $V$  and  $W$  are the pair nearest neighbor (NN) interaction and the trio interaction parameters, respectively. This hamiltonian can be derived as a model of strained epitaxy [15] and is essentially equivalent to the model of ref. [16]. Elsewhere we have shown that this model at low surface coverage can describe the formation of square  $2 \times 2$  plaquettes [15]. This may serve either as an oversimplified model of the self-assembly of quantum dots or as a model of chemical reaction between the lattice atoms having the 4-atom molecules as its product. Furthermore, at higher coverage the model exhibited a surface reconstruction [17]. All the phenomena listed take place at  $W > 0$  which physically corresponds to the positiveness of the elastic energy from which this term originates [15].

In the present paper we consider the case  $W < 0$ . Physically this may be justified in the case of strained epitaxy by considering the vacancies instead of atoms, *i. e.*, making in eq. (1) the substitution  $n_i \rightarrow 1 - n_i$ . We neglect the positive next NN (NNN) pair interaction appearing under this transformation by assuming that it is compensated for by an attractive NNN interatomic interaction. This assumption is made to keep the resulting hamiltonian as simple as possible, in the spirit of the renormalization group approach [7]. We stress once again that while we are unaware of any real system which would exactly correspond to the hamiltonian (1), a physically acceptable interatomic interaction potential and the lattice size misfit can be chosen so that the model described a plausible heteroepitaxial system. In view of possible application of the model in strained epitaxy, <sup>(3)</sup> below we consider the model where the “atoms” of the hamiltonian (1) are, in fact, the vacancies while it is the real atoms which are moving. We note, however, that simulations also were made with  $n_i$  being treated as atoms and no qualitative differences with the behaviour described below was found.

To study the kinetics of the model we consider an ensemble of atoms randomly deposited at time  $t = 0$  (the instant quench; see fig. 1a). The microscopic dynamics chosen was the activated atomic hopping which is a natural choice for the surface atoms [19]. The parameters in eq. (1) and the temperature were chosen so that

$$V/|W| = 0.75 \quad \text{and} \quad V/k_B T = 6. \quad (2)$$

We would like to stress that this choice does not correspond to any exact degeneracy because we consider an accidental degeneracy to be highly improbable in real systems. The glassy behaviour remains qualitatively the same if the value of  $V/W$  is slightly changed as well as if some weak additional interactions are present which do not change the most essential qualitative feature of the hamiltonian (1): the competition between the NN repulsion due to the pair interaction and the multiatom attraction within atomic trios. The minimum of  $H$  is unique and corresponds to a phase separated state of vacancies and atoms. Physically this corresponds to a partly filled epitaxial layer. The temperature was chosen to be high enough to allow us to follow the evolution of the system to the very end. At lower temperatures the CPU time scale quickly grows because of the “futile” dynamics similar to that described in ref. [20] when a small number of rapidly fluctuating particles hinders major rearrangements on broader scales.

Monte Carlo (MC) simulations were performed on finite-sized lattices of linear dimension  $L$  with periodic boundary conditions and the vacancy concentration  $c = 1/3$  which is below the percolation threshold which for the square lattice is 0.5 [21]. The time scale was normalized so that the hopping probability of a vacancy in the atomic bulk was equal to unity.

The evolution of the system proceeded as follows.

From eq. (1) with the above values of couplings it is easy to see that the vacancy lines consisting of more than four members have negative energy which caused their polymerization at an early stage of evolution.

With the advent of time these polymers start to branch and cross-link producing dendrimer-like structures (fig. 1b).

Then, at some finite time  $t_c$  the kinetic gelation of these polymers takes place. In fig. 2 the probability of a vacancy to belong to the gel fraction is shown together with the best fit to the critical curve of 2D percolation [21, 22]. In simulations the gel fraction was calculated in the standard way [21, 22, 23] for two sizes of the system  $L = 320$  and 500 and then interpolated to  $N = \infty$ . As we see, the agreement of the MC data with the theoretical values is not quite

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<sup>(3)</sup>In ref. [18] a long lived disordered wiggled vacancy structure in a partially filled wetting layer was observed. This might have been caused by the underlying glassy kinetics.

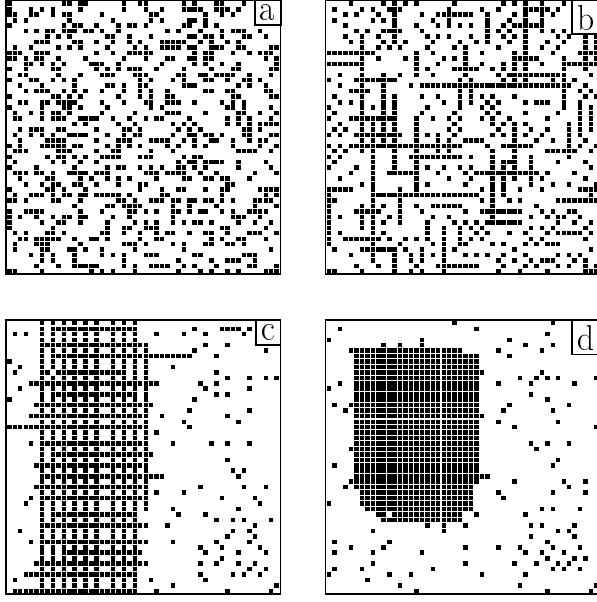


Fig. 1 – Snapshots of the system at different times of evolution: *a)*  $t = 0$ ; *b)*  $t = 5 \cdot 10^{-3}$ ; *c)*  $t = 1$ ; *d)*  $t = 1.5$ .

good but the problem of irreversible gelation is known to be difficult for simulation [22,23], so we invoke the notion of universality and the exactly known critical exponent  $\beta = 5/18$  [21,23] to retrieve the value of  $t_c \approx 0.018$  from our data.

In fig. 3 is depicted a typical configuration of vacancies in the gel phase. Noticeable is the cage structure characteristic of the glass state [1]. Furthermore, the structure seen in this figure is very close to a local energy minimum. A careful inspection shows that any allowed hop of a vacancy belonging to the gel fraction will lead to the energy growth while the movements

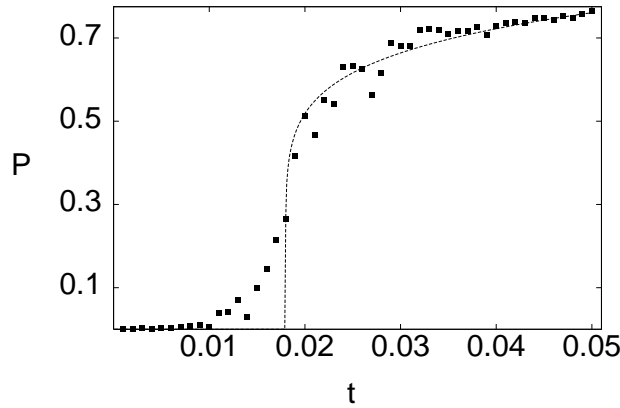


Fig. 2 – Percolation order parameter  $P$  (black squares) as a function of time elapsed since the initial random deposition; the dashed line is a least square fit to the universal critical dependence  $\text{Const}(t - t_c)^\beta$  [21].

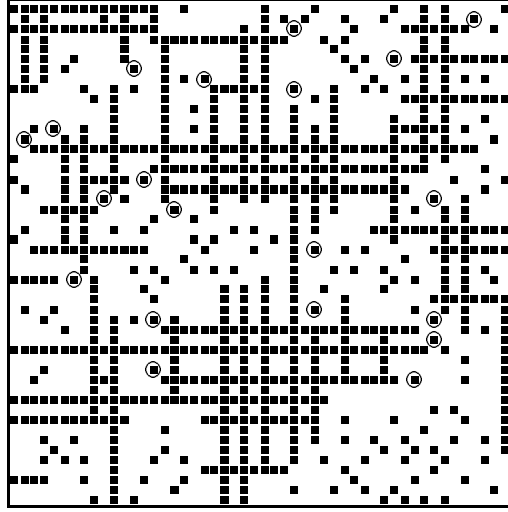


Fig. 3 – Typical local structure of the gel phase at  $\beta = 6$  and  $t = 0.05$ ; vacancies are shown by the black squares (only a  $50 \times 50$  block of the  $500 \times 500$  simulation box is shown). Enclosed in circles are the “active” vacancies which at the next hop can become attached to the nearby polymer chain.

of those that do not belong to the gel leave the energy constant in the majority of cases. Some movements of the free vacancies also augment the energy and only the 20 “active” ones which we enclosed in the circles can diminish the energy by attaching themselves to a nearby polymer chain. Thus, the system is quite close to a minimum of the energy landscape [1,3] but is not at the bottom of it. On the other hand, one can find in fig. 3  $N_a \approx 60$  “active” polymer ends which we define as those with the smallest detachment energy  $\Delta E_{\min} = -(W + V)$  [see eq. (1)]. Because the vacancy as a rule has 3 neighboring sites to hop, the number of detached monomers can be estimated as

$$N_d = 3N_a \exp\left(-\frac{\Delta E_{\min}}{k_B T}\right) = 3N_a \exp\left(\frac{W + V}{k_B T}\right).$$

Substituting  $(W + V)/k_B T = -2$  from eq. (2) we get

$$N_d \approx 24.$$

Thus, the number of active monomers approximately corresponds to its equilibrium value which means that the system is close to a minimum of the free energy  $F$ . This explains its relative stability because the thermodynamic driving force proportional to  $\delta F$  is close to zero.

The local autocorrelation function

$$g(t, t_w) = \frac{1}{Nc(1-c)} \sum_i [\langle n_i(t + t_w) n_i(t_w) \rangle - c^2] \quad (3)$$

is plotted in fig. 4 for several values of the aging time  $t_w$ . Because of much larger time intervals, the simulations were performed on systems of size  $L = 50$  with averaging over 100 realizations. At equilibrium  $g(t, t_w)$  should be  $t_w$ -independent while in our case relaxation considerably slows down with age. Noticeable also is the separation of time scales characteristic of glassy

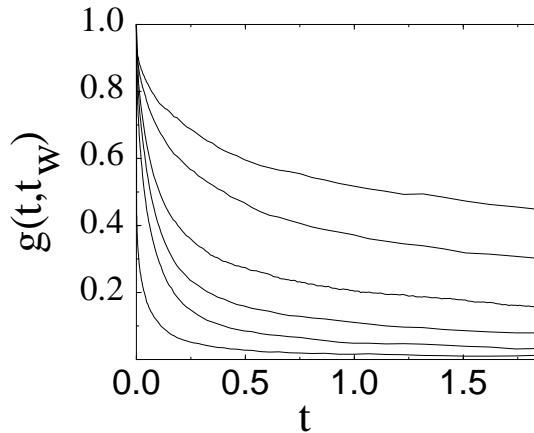


Fig. 4 – Autocorrelation function eq. (3) shown (from bottom up) for  $t_w = 0, 0.01, 0.05, 0.1, 0.25$ , and  $0.5$ .

state: quick relaxation at early times and much slower one at later stages of evolution (the so-called  $\beta$ - and  $\alpha$ -processes [1]).

Further aging leads to the compactification of the gel fraction which at its late stages leads to a transient ordered state [24] (fig. 1c). Finally, the system arrives at its equilibrium phase separated state which can be interpreted as the glass crystallization (fig. 1d).

Kinetic glassy phenomena are known to be extremely sensitive to such parameters as temperature and the cooling rate. For example, the so-called escape time  $\tau_{out}$  [1] corresponding roughly to half the time needed for the glass to crystallize (in our case for the atoms and vacancies to separate) was in our simulations with the instant quench approximately two orders of magnitude greater than  $t_c$ . Under a step annealing, on the other hand, we were able to achieve  $\tau_{out} = O(t_c)$ .

Thus, we have shown that the model with the hamiltonian (1) exhibits a glass transition of the type of the kinetic gelation of lattice polymers [21, 22, 23]. The transition is of the second order, so we may hope that the universality hypothesis apply. This means that in the vicinity of the critical point  $t_c$  the behaviour is insensitive to the microscopics of the system and should be the same as in the off-lattice case. Furthermore, if the universality class of the glass transition is unique, than the universal behaviour should be the same in all systems mentioned at the beginning of this paper. This seems to be too daring a conclusion because physically polymers and, *e. g.*, metallic glasses look extremely disparate. However, off-lattice numerical simulations of refs. [25, 26] showed that indeed in the vicinity of the glass transition both systems look very much alike. Moreover, even at the microscopic level the real space Adam-Gibbs [27] (see also ref. [28] and references therein) cooperative structures in an off-lattice Lennard-Jones liquid look similar to the polymers of fig. 1b. This is yet another argument in favor of the hypothesis that the proposed model may really describe a universality class of the glass transition in 2D liquids.

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